THE CHEMICAL COMPOSITION OF THE ESTHONIAN M.-ORDOVICIAN OIL-BEARING MINERAL „KUKERSITE“

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Introduction.

1. Geological position.

The oil-bearing minerals, known as „kukersite“ and dictyonema-shale, form two layers of the Cambrian and Ordovician strata in the North of Esthonia. The minerals are usually called „oil-shales“ and the term „shale“ is here used merely for convenience, for the kukersite is not a true shale. The seams of oil-shale are well developed along the southern coast of the Gulf of Finland. The bedding of these seams is nearly horizontal with a slight dip to the South West.

The Cambrian strata consist chiefly of sandstone and clay, but the Ordovician strata are formed of sandstones, Dolomites and Marly Limestones. At the base of the Ordovician strata lies the so called dictyonema-shale, dark brown or black in colour.

The more important from the industrial point of view is kukersite, which lies in the Middle Ordovician strata. The name „kukersite“ is derived from that of the village „Kukruse“, in the vicinity of which F. Schmidt collected and investigated the fauna of the above mentioned seams. (F. Schmidt „On the Silurian and Cambrian Strata of the Baltic Provinces etc.“ Quart. Journ. of the Geol. Soc. Vol. XXXVIII (1882)).

In the Kohtla and Vanamoisa districts the shale lies very close to the surface and it is worked in open quarries.

The calculated amount of kukersite is very considerable. According to Paltshinsky it may be 40 to 50 thousand million tons. (H. Bekker: „New Bryozoa from Kuckers stage in Esthonia“, Ann. & Mag. of Nat. Hist. Sec. 9 Vol. IV. 1919 p. 328).

More recent calculations give figures much lower. According to H. v. Winkler the total quantity of kukersite is about 128,790,000 tons. (H. v. Winkler: Über Umfang und Abbau-

würdigkeit estländischer Bodenschätze. Mtl. a. d. Geol. Institut der Univers. Greifswald III (1920) p. 15). The immediate available supply of oil shale is estimated by the Esthonian government at 1,500,000,000 tons. (Quart. Colorado School of Mines, 16, 2, 1921).

2. Bibliography and review of the research work before 1920.

The kukersite was first found in the neighbourhood of Kohala by Engelhardt in 1789. On this discovery Georgi reported to the „Free Economical Society" of St.-Petersburg in 1791. (Georgi: „Von einer feuerfangenden Erde aus der Revalschen Stadthalterschaft". Auswahl ökonomischer Abhandlungen welche die freye ökonomische Gesellschaft in St.-Petersburg in teutscher Sprache erhalten hat. 3. Bd. 1791).

Seven years later Georgi described the kukersite as „a brown clayish or marly bituminous earth" (Bergpecherde). „It burns with flame without giving an unpleasant odour. Ten ounces of this earth contain 4 ounces of tar and 25 grains of common salt. Darker kinds, finely ground, are used as a substitute for umber". (Georgi: Geographisch-physikalische und Naturhistorische Beschreibung des Russischen Reichs 3. Th. Königsberg 1798 p. 333—334).

Helmersen was the first to subject the kukersite to destructive distillation. Results of his trial are given below:

160 lbs. of shale yielded 9.25 lbs of Tar and 7.75 lbs of Pitch.
40 lbs of shale yielded 80 cu. ft. of gas.

(Helmersen: „Der in Estland bei Fall und Tolks entdeckte brennbare Schiefer", Inland 1838 p. 769 and „Über den bituminösen Tonschiefer und ein neuentdecktes brennbares Gestein der Übergangsformation Estlands etc." Bull. Sci. publié par l'Académie Impériale des Sciences de St.-Pétersbourg T. 5. 1839).

The shale used by Helmersen had the following proximate composition:

Volatiles	70.06%	sp. gr. 1.28
Coke	11.08 „	
Ash	18.76 „	

In 1850 Prof. Petzhold, and in 1870 A. Schamarin, at Dorpat University analysed different samples of shales, giving special attention to the mineral constituents of the shale.

A tabulated list of A. Schamarin's results contains excellent information relating to the composition of the ashes of the shale and shews a great variation in the percentage of the principal components. With regard to the organic matter of the kukersite Schamarin gives an average ultimate composition as follows:

Table I. Ultimate Composition of Shale.

On dry raw shale		On ashless organic matter.
C	— 29.76%	C — 70.52%
H	— 3.07 „	H — 7.21 „
N	— 0.12 „	N — 0.29 „
O	— 9.25 „	O — 21.98 „
Ash	— 37.25 „	
$CO_2 + H_2O$	— 20.66 „	

The shale was previously treated with hydrochloric acid and dried at 140° C.

Table II. The Average Yield of Gas, Coke and Tar.

	Percentage.		
	Gas	Coke	Tar & oils.
Original shale	19.72	8.60	28.86
Pure organic substance	34.17	14.50	50.09

(A. Schamarin: Chemische Untersuchung des Brandschiefers von Kuckers. Archiv f. Naturkunde Liv-, Esth- und Kurlands I. Ser. B. 5. 1870).

In 1871 R. Hehn analysed the distillation products of kukersite with the following results:

Table III. Analysis of Shale.

$CaCO_3$	18.41%
$MgCO_3$	0.12
Al_2O_3, Fe_2O_3	0.33
Silicates	17.90
Bitumen	60.33
SO_3	0.03
H_2O	2.20
	99.32

The distillations were carried out: I in a small cast iron retort, II and III in a gas-retort.

Table IV. Percentage Yield of Oil and Coke.

	I	II	III
Oils	12.9	15.6	20.0
Coke	66.6	52.9	44.6
H_2O	10.1	7.8	} 25.2
Volatile oils & losses	10.4	23.7	

Table V. Fractionation of Oils. Expt. I.

B. P.	% Yield.	Sp. Gr. at 10° C.
70°—120° C	11.5	0.763
120°—160°	5.5	0.800
160°—180°	7.5	0.822
180°—240°	23.0	0.862—0.903
240°—300°	20.4	0.862—0.956
Residue	32.2	

Expts. II & III.

B. P.	% Yield		Sp. Gr. at 10° C.
in °C	II.	III.	
70°—120°	7.3	5.3	0.797
120°—160°		13.3	0.808—0.863
160°—180°	13.7	9.3	0.889
180°—240°	11.0	29.9	0.912—0.943
240°—300°	24.3	28.7	0.956—0.978
300°—320°		13.4	0.991

Table VI. Ultimate analysis of Oils: (Expts. I, II. & III.).

B. P.	Sp. Gr. at 18° C	% C	% H	% O	Remarks
70°—120°C	0.749	81.76	12.85	5.39	
120°—160°	0.778	82.71	12.77	4.52	
160°—180°	0.806	83.48	12.35	4.22	
180°—210°	0.838	83.84	11.22	4.91	From 180° C the oils shew fluorescence.
210°—240°	0.871	84.54	11.50	3.86	
240°—265°	0.900	83.39	11.39	5.22	
265°—300°	0.923	85.53	10.87	3.60	

(Hehn: Die Produkte der trockenen Destillation des Brandschiefers aus Kuckers. Balt. Wochenschrift IX. 2 & 3 1871 and H. v. Winkler: Petroleum XV N. 6 1919.)

The investigation of Kukersite was again taken up after a period of 40 years by L. F. Fokin. His paper on „The Structure and Products of Decomposition of Esthonian Bituminous Rocks" appeared in the Russian Mining Journal (Горный Журналъ Gorny Journal) 1913 V. II. p. 117 etc.

According to Fokin, the colour of raw shale is due to the mineral matter, and varies from yellowish brown to dark brown.

Sp. gr. 1.6 for 50% of organic matter in shale,
„ „ 1.23 „ 74% „ „ „ „ „

On exposure to the air the shale undergoes slow oxidation, indicated by a deepening in colour.

Fokin first tried the action of different solvents on shale. He found „The total amount extracted by solvents (alcohol, ether chloroform, benzene, carbon disulphide, carbon tetrachloride, acetone, benzine and pyridine) of tarry, amber-yellow oil (forming a thin film after removal of solvent) did not exceed 0.1% of the organic matter".

To isolate pure organic substance from the mineral matter, Fokin treated the shale successively with hydrochloric and hydrofluoric acids at a moderate temperature. In this way he succeeded in reducing the ash contents in the organic substance to 0.4%. A nearly pure organic substance appeared as a light-yellow powder (sp. gr. 1.07—1.145) darkening in contact with air.

Above 250° C this organic substance, isolated from the shale decomposed with evolution of gases, but did not melt. On distillation the decomposition begins at 250° C and from 80 to 85% is carried over as permanent gases, water vapour, and other condensable products. The residue is carbon.

With regard to the chemical character of the oils obtained by distillation of shale, Fokin says: „All the predominant oils have a paraffinic and unsaturated aliphatic structure; absence of benzene derivatives characterizes the products of distillation. The light oils contain olefines and paraffins in approximately equal quantities, the middle fractions up to 225° C have an acid character; higher fractions absorb oxygen, giving oxidation products, without elimination of free carbon".

During the Great War (owing to the shortage of fuel in

Russia, especially in the Petrograd district) a Fuel Committee was established in Petrograd. The Committee investigated also the methods of utilization of Esthonian shales. A full report on „The Baltic Oil Shales" was issued in Petrograd in 1919 by N. F. Pogrebov, a member of the above mentioned Committee. The report does not add much to the knowledge already obtained by previous investigators, except in regard to the geological information and an account of some commercial trials. A great number of approximate analyses is given; these shew great variation both in the methods employed and in the results obtained. One large scale trial described shews the suitability of kukersite for gas production.

The distillation was carried out in an old type horizontal retort plant at 1000° C.

Yield of gas: 2.5 m^3 per kilogram of air-dry shale. Sp. gr. of the gas 0.6 (air — 1). Calorific power 4900—5000 cals.

Table VII. Analysis of Gas.

CO_2	16.1 %
C_nH_{2n}	6.5 „
O_2	0.6 „
CO	13.9 „
CH_4	28.2 „
H_2	32.2 „
N_2	2.5 „
NH_3	0.15 „

Sulphur	12.95 grammes in 100 m^3.
Tar	5% of weight of raw shale.

The tar is rich in naphthalene.

Finally a report on a trial with Esthonian shales appeared in the Petroleum Times (Vol. V, N. 119 1921 p. 432). It shews that 65.23 gallons per ton of crude oil was obtained from the shale. Average spec. gr. of the oil was 0.918. The shale as a source of spirit and oil production is extremely valuable.

Experimental.

The different results obtained by different workers are not only due to the difference in chemical nature of the original shale, but also to the methods employed. No definite information has been given either as to the nature of liquid distillates, obtained by destructive distillation or of the effect of temperature upon the yield of oils and gases. In order to examine the previous research work, bring the analytical data up-to-date, and investigate the effect of temperature and methods of distillation on the thermal decomposition of kukersite, the author carried out a series of experiments in the Fuel Laboratories of the Imperial College of Science and Technology, under the direction of Prof. W. A. Bone, F. R. S.

A. Proximate and Ultimate Analyses.

Moisture in Raw Shale. — The moisture content of raw shale varies considerably from seam to seam, it depends also upon the hygroscopic condition of the atmosphere, but on an average does not exceed 35%. In June, 1920, the amount of moisture was determined on the spot in the Kohtla quarries. The results are given below:

Table VIII. Moisture in Raw Shale.

No. of seam	Moisture content
I	30—40%
II	26—32 „
III	13—19 „
IV	16—19 „

The raw shale easily loses hygroscopic water and air-dry samples rarely contain more than 7% of water.

Moisture in Air Dry Shale. — The exact determination of moisture in air-dry shale is complicated by the presence of occluded gases. R. Jannsen proposed to dry shale for 1 hour at 90° C „to avoid the losses due to the destructive distillation which begins at 100° C". (R. Jannsen „Märkused kukersiidi proovimetoodide kohta" — Notes on the methods of Analysis of kukersite. E. T. S. Ajakiri N. 15—16 (1920) Journ. of the Esthonian Technical Society in Reval).

The author dried three 5-gram samples of shale:

(a) at 105° C for 1 hour;

(b) at 60° C in vacuum desiccator for 1 hour;

(c) in vacuum desiccator over concentrated sulphuric acid for 24 hours at room temperature.

Samples (b) and (c) gave approximately the same result, average 2.10%, (a) shewed a slightly higher result, viz., 2.38%.

In the case of samples from seam III, no difference was observed between the determinations of moisture at 105° C and in vacuo.

In subsequent experiments the shale was dried in vacuo (as in (c)).

Ash. The Ash contents of Esthonian oil shales lie approximately between 20—50% and the composition of the ash varies considerably in different samples. From 200 samples analysed in Petrograd and Reval the following limits were obtained:

Table IX. Range of Composition of Ash.

SiO_2	18.9 % — 55.7 %
Al_2O_3, Fe_2O_3	2.2 „ — 45.3 „
CaO	5.4 „ — 55.0 „
MgO	0.35 „ — 8.5 „
SO_3	0.96 „ — 12.1 „
P_2O_5	0.34 „ — 1.80 „

In samples of shale taken by the author from 4 different seams at Kohtla and analysed at the Imperial College the ash contents are as follows:

Table X. Percentage of Arh.

I seam	29.6%
II „	48.4 „
III „	35.4 „
IV „	29.5 „

The determination of ash was carried out on the principle adopted for coal analysis in the Fuel Laboratory of this College.

5 gm of shale was put into a muffle furnace at a temperature of 650°—700° C and left for 45 minutes, taken out, stirred and heated again for 45 minutes, cooled and weighed.

In the Kunda Cement Factory, Esthonia, the determination of ash in Kukersite is carried out in two stages: (i) determination of carbon dioxide (volumetrically) and (ii) heating to constant weight (see R. Jannsen loc. cit.).

Volatile matter. — 20 gm of dry shale was weighed out into a No. $3^1/_2$ Morgan Fireclay crucible (the crucible had previously been heated to redness in a muffle and allowed to cool in a drying chamber). The covered crucible, containing the shale, was put into a muffle furnace the temperature of which was maintained at 900° C. Heating was continued for 5 minutes after the evolution of inflammable gases had entirely ceased. The crucible was allowed to cool and weighed again.

This method causes a loss of carbon dioxide. Therefore the amount of CO_2 which could be liberated by hydrochloric acid was determined in raw shale and in the residue from the determination of volatiles. It was found that about 2/5 of the total CO_2 was lost by heating at 900° C.

R. Jannsen used for the determination of volatiles in Kukersite the Finkener method adopted in Berlin (Heinrichsen & Taszak: (i) Glückauf 1908 p. 1325, (ii) Mitt. d. Kgl. Mtpra. Berlin 1912 p. 453). The experiment is carried out in a current of hydrogen: (1) for 15 minutes the air is displaced by hydrogen without heating; (2) the CO_2 is given of at low temperature (another 15 mins); (3) the crucible is heated on „full flame of Bunsen burner“ for 45 minutes.

This method is very laborious and not quite exact because the term „full flame of Bunsen burner“ does not indicate any constant temperature. As will be seen below, the percentage of volatiles is a function of the temperature.

Table XI. Results of Crucible Test.

No. of seam	Yield of volatiles %	Character of residue
I	58.4	Powder
II	50.7	do
III	51.8	Very-porous, slightly coking
IV	56.9	do

Ultimate composition. — The ultimate composition of the kukersite used in all the experiments is as follows:

Table XII. Ultimate Composition.

C	71.58%
H_2	7.40 „
N	0.48 „
S	1.50 „
O_2	19.04 „

Calculated on the pure dry organic substance.

It is worthy of notice that the ultimate composition of the pure organic substance is approximately constant for different kinds of Kukersite.

B. The Action of Solvents on Kukersite.

As previously mentioned, L. Fokin first tried the action of solvents on kukersite, but the amount of extract did not exceed 0.1% of organic matter. It has been found in the Fuel Research Laboratory of I. C. S. & T. that the extraction of coal with solvents in a Soxhlet apparatus yields a slightly higher percentage of extracts than extraction in a reflux.

An improved form of Soxhlet apparatus as used in the Fuel Research Laboratory was employed for the extraction of shale. About 10 gm of shale, atmosphere of nitrogen.

Table XIII. The Results of Extraction.

Solvent	Hours	%	Colour	Remarks
Acetone	120	0.27	Light yellow	
Chloroform	120	0.22		
Benzene	124	0.43	Orange with green fluorescence	
Carbon Di-sulphide	100	0.49	Yellow	
Petroleum Ether, B. P. 60°—80° C	119	0.49	Nearly colourless	
Toluene	124	0.52		
Xylene	120	0.77	Yellow	
Pyridine*)	48	0.70	Dark red	Probably decomposition occurred. Residue black.
Tetrachlorathane	70	2.20	Dark brown	Decomposes shale. Elimination of HCl.

*) Pyridine remored from extract (i) by distillation under reduced pressure (ii) precipitation by HCl—aq. (1 : 1).

Results calculated on pure organic matter.

The greater part of the extract was obtained during the first 2 days and after 5 days the extraction may be regarded as complete. The derivatives of benzene yield higher percentage of extract the higher their boiling points.

Carbon disulphide and petroleum ether yield approximately the same results. Pyridine and tetrachlorethane are not true solvents, especially the latter. Experiments were carried out to investigate the effect of an electrolyte on the dissolving power of a neutral solvent (non-electrolyte). The solvent used was benzene and about 2.5% of glacial acetic acid was added. The shale powder was moistened with the acid before extraction in a reflux apparatus. No difference was observed: the percentage of extract was approximately the same, whether acetic acid was present or not.

Table XIV.

Solvent	%	Hours	Colour
Benzene	0.26	24	Orange
do with 2.5% of acetic acid	0.28	24	do

C. The Action of Reagents.

Potassium Hydroxide. — Fokin in his paper stated: „The organic substance of the shale by treatment with alkalies loses about 11% of its weight". The author boiled finely powdered kukersite with a 20% solution of potassium hydroxide for 1 hour in a reflux apparatus (200 cc of KOH and 10 gm of shale). On cooling a pale yellow solution was obtained. The filtrate was neutralised with hydrochloric acid and on standing a white precipitate formed. The weight of the precipitate did not exceed 4% of the shale taken.

Acids. Hydrochloric acid of 40% strength removes the greater part of the mineral matter. Conc. mineral acids all decompose the kukersite.

D. Action of Heat.

Initial Decomposition. — Many of the earlier investigators assumed that the destructive distillation of kukersite begins at a temperature as low as 100° C., and R. Jannsen recently proposed to dry kukersite at 90° C. „to avoid loss by distillation, which begins at 100° C". They all seem to have been misled by the escape of occuded gases. To determine the temperature at which initial decomposition takes place the following experiments were made: 10 gms. of shale were put into a small distillation tube connected to a condenser and a gasholder. An electric tube furnace was employed. Before heating, the whole apparatus was partially evacuated. The temperature was slowly raised to 180° C (1 hour), but no signs of distillation

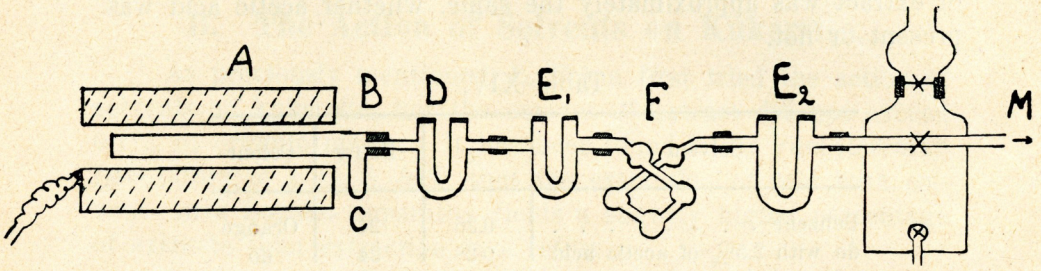

Fig. 1. A — electric furnace, B — distillation tube: about 45 cm long, 2 cm wide; C — side tube (for oil): $^3/_4$ cm wide, 3 cm from the open end of Distill. tube; D—U-tube, as a condenser for volatile oiles, E_1 & E_2 — $CaCl_2$-tubes, F — Liebig sulphuric acid bulb, G — gasholder.

were observed. At 250° C a marked evolution of gases began which practically ceased after 6 hours. During the heating the temperature varied between 250° and 255° C. 27 cc of gas (at 0°, and 760 mm) were obtained and a few drops of colourless oil with a sweet ethereal odour stuck to the walls of the distillation tube. The gas obtained contained (excluding air) 8.7% CO_2, 0.6% heavy hydrocarbons and 13.7% CO. The residue (of the the gas) did not explode with oxygen.

Distillation at Various Temperatures. — For distillation tests up to 700° C a glass tube was employed, at 900° C a silica tube. During the first series of experiments an acid bulb was placed between U-tube and gas holder to determine the amount of ammonia. (See Fig. 1). Charges of 20 gm of shale were treated.

A. The electric furnace was heated previously up to the desired temperature and the same temperature maintained throughout the experiment. Duration of distillation 2 hours. The whole apparatus was partially evacuated. The distillation tube was gradually introduced into the furnace. After the first hour the greater part of the kukersite was decomposed.

The conditions in this operation approximate very close to the conditions existing in actual practice. The method was found to be an excellent one for distillation at low temperature. At 900° C the evolution of gases, in spite of the care taken, was so violent that the shale particles were projected to the outer end of the distillation tube. In distilling by this method the cracking of the oils is unavoidable.

Table XV. Results of Distillation. Expt. A.

Temp. °C	Percentage yield	Yield of oil Gallons per ton	Yield of gas cu. ft. per ton at 0°, & 760 mm	Yield of Ammonia	Calorific values of crude oils in B Th. Us. per lb.
410	27.1	63.3	1900	—	—
500	29.7	72.9	2250	—	17028
600	30.8	74.8	3000	0.02%	17428
700	27.5	65.0	4500	0.04 „	—
900	21.7	49.7	7200	0.11 „	—

The yield of oil increases as the distillation temperature rises, but reaches a maximum at about 600° C; above this temperature the yield of oil decreases and the yield of gas increases with the rise of the temperature.

In a paper „The Distillation of Lignite at Various Temperatures" A. Naumann tried to shew that the amount of tar and gas yielded at various temperatures increases with increase of temperature.

At 450° the quantity of tar was 12%
„ 960°—1000° „ „ „ „ „ 19 „

(Z. f. Elektrochem. 1916. 22. 109).

The difference in results can easily be explained by the fact that a different method was used in the case of Lignite,

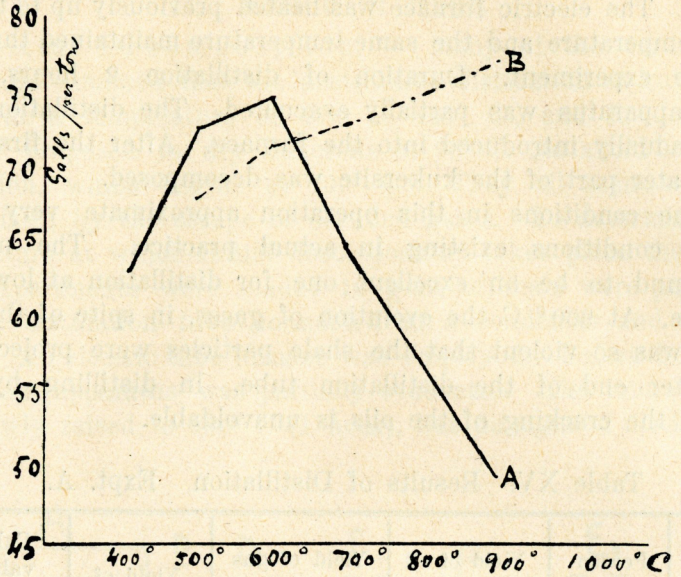

Fig. 2.

Yield of Oil: *A* — in expt. *A*, *B* — in expt. *B*.

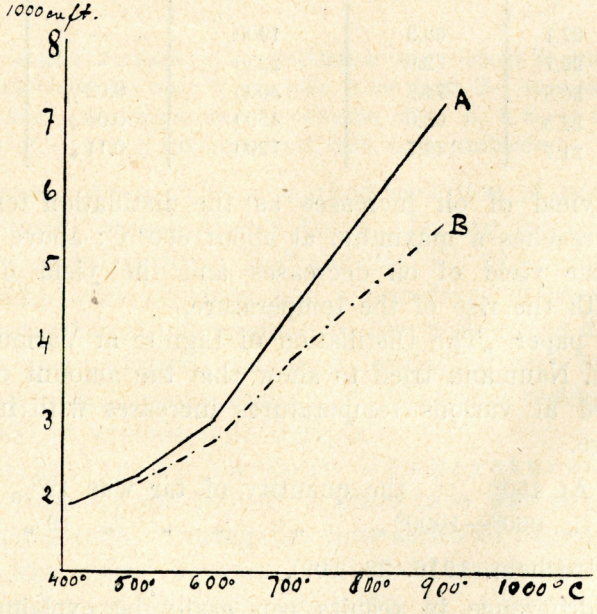

Fig. 3

Yield of Gas: *A* in expt. *A*, *B* — in expt. *B*.

viz., a gradual increase of temperature up to the required temperature of distillation.

B. To prove this the following experiments were carried out. The temperature of the electric furnace was slowly raised from 200° C to 900° C in the course of 2 hours, after which period the temperature was maintained at 900° C for 1 hour. The rate of increase of the temperature was 5° C to 6° C per minute. The silica distillation tube was inserted to its full extent in the furnace at 200° C. This method of operation is very like that described by Thomas Gray and J. G. King in their paper on „The Assay of Coal for Carbonisation Purposes", (Fuel Research Board: Tech. Paper N. 1, 1921), but the conditions are quite unlike those existing in actual practice.

Table XVI. Results of Distillation. Expt. B.

Temp. ° C	Percentage-Yield	Galls. of oil per ton	Cubic ft. of gas per ton at 0° C & 760 mm
500	27.8	68.0	2170
600	29.3	71.5	2720
700	30.8	73.7	3810
900	33.0	77.3	5650

The experimental results given in Table XVI differ from those given in Table XV. Table XVI shews that the yield of oil increases with increase of temperature of distillation. The amount of gas obtained (Table XVI) by distillation does not increase at the same rapid rate with the rise of temperature.

Table XVII. Analysis of the Gases. Expt. A.

Gas	Temp. 500° C	600° C	700° C	900° C
H_2S	—	2.1	2.2	—
CO_2	22.5	19.6	15.6	7.4
C_nH_{2n}	28.2	24.8	22.0	20.2
CO	9.3	11.2	12.5	16.4
CH_4	34.0	26.6	19.6	12.9
H_2	4.2	10.8	22.9	33.0
N_2	1.8	7.8	5.2	9.1
Calorific values calculated in cals per cu. ft (gross)	232.9	204.6	182.3	171.0

Air is excluded.

The calorific value of the original dry shale, 4410 KCUs, was determined in a bomb calorimeter.

E. Liquid Distillates.

It is well known that the liquid distillates from a given fuel vary greatly in character dependent on the temperature and the manner of distillation. In all earlier investigations on kukersite no exact information is given as to the temperature of distillation or the manner of heating; analyses of tars given by different investigators vary considerably. It appears that great difference exists between the products obtained by distillation of coal, lignite, etc., at low temperature and those obtained at high temperature.

The low temperature tar may be regarded as a primary product of decomposition (W. A. Bone: Coal & Its Scientific Uses. p. 133).

For the distillation of shale on a larger scale the author used an iron retort provided with a condenser. Charges of 1 kg of shale were treated. The temperature of the furnace was observed by means of a Foster pyrometer. The distillation was started at 450° C & the temperature of the furnace gradually raised to 550° C at which temperature the retort was maintained for 2—3 hours.

In one case the final temperature was raised to 600° and a larger yield was obtained. The following are particulars of the experiment:

Charges taken, 1 kilo of shale.
Duration of heating $2^1/_2$ hrs.
Weight of tar & water 230 grams.
Weight of residue 540 gms.
Weight of gas & loss 230 gms.

Analysis of Crude Tar. Two samples of tar were analysed. One obtained by the distillation of the kukersite in a semi-large vertical retort plant at Reval (Esthonia) with superheated steam (450°—500°), another distilled at 550° in a small cast-iron retort at the Imperial College, Sth. Kensington

Sample I.

The crude tar was a dark brownish liquid with slight green fluorescence, sp. gr. 0.939 at 17° C, the ultimate composition of which was: C — 80.9%, H — 10.6%, S — 0.3%, O — 8.2%. This analysis is very like one of a shale oil from Ardèche. (Sir B. Redwood: Petroleum V. I p. 223).

Steam distillation was applied to remove light oils. Steam carried over 28.5% (by volume) of light greenish yellow oil of sp. gr. 0.795 at 17.5° C. After washing with conc. sulphuric acid, sodium hydroxide and water the light oil lost 17% of its volume. (200 cc. of light oil was treated with 30 cc. of conc. sulphuric acid followed by 100 cc. of 15% sodium hydroxide).

Two samples of the light oil were fractionated: (i) without previous washing with conc. sulphuric acid, and (ii) after a treatment with conc. sulphuric acid.

Table XVIII. Results of the Fractionation.

Temp.	% Yield. i	% Yield. ii	Sp. gr. at 17° C	Colour
Up to 120° C	22.1	16.0	0.761	Colourless
120°—150°	30.0	21.3	0.776	
150°—175°	18.6	22.6	0.789	
175°—200°	19.2	18.2	0.808	Light yellow
above 200°	10.1	21.5	0.868	Orange

On treatment with conc. sulphuric acid the oils of lower boiling points were attacked more rapidly.

Estimation of Unsaturated Compounds in Crude tar. For the analysis of crude low temperature tar one of the methods adopted for the analysis of crude oil (petroleum) was employed.

A preliminary test shewed that it is quite impossible to absorb the whole of the unsaturated hydrocarbons directly by conc. sulphuric acid as in the method used for the analysis of petroleum (C. Engler: Das Erdöl I. Bd. p. 499. 1912). A dark emulsion was formed and no separation into layers was obtained after standing for 24 hrs.

The following method was found to be quite satisfactory: The original crude tar was mixed with pure Caucasian benzine

which had been previously treated with conc. sulphuric acid to remove any unsaturated hydrocarbons. The tar was dissolved in an equal volume of benzine and the absorption carried out until no change in volume appeared. Finally, to remove the last traces of unsaturated compounds, conc. sulphuric acid containing 20% of sulphur trioxide was used, care being taken to prevent overheating of the mixture. The total amount of unsaturated compounds determined by this method was 94.5%. The residue was treated with conc. nitric acid, but no appreciable decrease in volume occured. The light oil from the steam distillation contained about 60% of unsaturated compounds viz., open chain compounds.

Different methods are suggested for the determination of aromatic constituents and paraffins in hydrocarbon mixtures. The liquid sulphur dioxide method seems to work well, but it is not applicable if the content of aromatics exceeds a limit of about 25%. (Met. & Chem. Eng. XIII N. 12. 1915. p. 713 and Vol. XVIII N. 8 p. 396.)

Valenta's method based upon the separation effected by dimethyl sulphate lacks value in the matter of quantitative accuracy. (Rittman, Twomey & Egloff Met. & Chem. Eng. p. 682. Vol. XIII N. 10.)

In order to determine the aliphatic or cyclic character of the unsaturated constituents Nastukov's reaction was employed. (Engler: Das Erdöl Vol. I. p. 554 & also Chem. Centralbl. 1904. II 1042).

After a few preliminary tests the following method was adopted: 28 gm. of crude tar was mixed with 60 cc. benzine; 30 cc. of conc. sulphuric acid was carefully added without shaking; 20 cc. of 40% formaldehyde was dropped into the mixture. The flask was cooled in ice-water & slightly shaken until all the formaldehyde was added. The shaking & cooling were continued until no heat formation was observed. The mixture was left for half an hour to settle and then poured into ice-water and neutralised with ammonia. The precipitate was separated from the liquid by means of a Buchner funnel and washed with benzine and hot water. The washing alone does not remove all resinified hydrocarbons from the condensation product which is called „formolite". The precipitate was dried at 105° C for 1 hr. and refluxed with benzine for half hour to

remove the last traces of resinified hydrocarbons from the formolite. After drying a yellowish brown powder was obtained.

The formolite index was 74, hence the quantity of cyclic unsaturated hydrocarbons in the crude tar is 55.5%. The heavy oil from the steam distillation (sp. gr. 0.984 at 17° C) contained 77% of unsaturated cyclic compounds.

Sample II.

The sample of crude tar obtained by distillation of kukersite in the small iron retort was very similar to that of sample I but its specific gr. was lower; 0.911 at 14.4° C.

A. Steam distillation was applied to remove light oils. Steam carried over 31.8% (by weight) of light greenish yellow oil, sp. gr. 0.790 at 65° F (18,3° C). The following are results of fractionation of the light oil:

Table XIX. Fractionation of Light Oil.

Temp. in ° C	Percentage yield	Sp. grav. at 65° F	Colour
Below 120	20.4	0.7441	Colourless
120—160	40.9	0.7800	Pale yellow
160—200	24.9	0.8123	
above 200	13 8	0.8457	Orange

The heavy oil, sp. gr. 0.988 at 65° F (18·3° C) was also fractionated under atmospheric pressure.

The results are given below:

Table XX. Fractionation of Heavy Oil.

Temp. in ° C	Percentage yield	Sp. grav. at 65° F	Colour
Below 200	2.7	0.864	Orange
200—300	22.0	0.910	Reddish braun
300—330	20.2	0.950	do
above 330	55.0	soft pitch	Black

B. Another sample was distilled under reduced pressure. In the first experiment 454 gm of tar was distilled in a $2^1/_2$-litre

distillation flask; in the second experiment 270 gm in a 2-litre flask. A Liebig condenser was used in both cases.

The results of distillation are given below:

Table XXI.

B. P.	Pressure in mm	% Yield of Oil
Up to 100° C	75	23.4
100°—170°	55	32.2
170°—245°	45	14.5
245°—300°	35	15.4
above 300°	—	14.4

The oils of the same boiling points were mixed and re-fractionated under reduced pressure using a 500 cc Jena flask provided with a Young (4 bulbs) still head.

Table XXII shews the results of fractionation and some physical and chemical properties of the oils.

Table XXII. Distillation of Oil.

B. P.	Press. mm.	%	Colour	Sp. gr. at 14.4° C	Refract. indices at 13.6° C	Acid No.
Up to 50° C	55	11.4	Pale yellow	0.766	1.4275	—
50°—100°	35	24.0	Orange	0.823	1.4541	4.0
100°—125°	35	8.4	Red	0.877	1.4793	7.5
125°—150°	32	7.1	Orange	0.888	1.4863	5.8
150°—175°	30	11.3	Reddish orange	0.928	1.5068	7.2
175°—200°	35	7.9	do	0.977	1.5324	6.3
200°—225°	35	6.6	Red	1.001	1.5445	5.1
225°—250°	30	6.7	Dark red	1.010	1.5579	—
250°—270°	30	4.6	do	1.028	1.5651	—
above 270°	—	12.0	Black	semi solid pitch.	—	—

The refractive indices are given as an average from 2 determinations. Sp. gr. of the first three fractions were determined by means of an aero-pyknometer, of all other fractions by means of a sp. gr. bottle.

The free acid was determined by the American method

and acid numbers give the milligms of KOH required to saturate the free acid in 1 gm of the oil. (W. A. Hamor & F. W. Padgett, The Technical Examination of Crude Petroleum & c. p. 96).

F. The Origin of Kukersite.

Palaeobotanist M. Zalessky examined microscopically a large number of sections of kukersite. (Zalessky M. Sur le sapropélite marin de l'age silurien formé par une algue cyanophycée. Year Book of Russ. Palaeont. Soc. Petrograd. 1917 Vol. I. p. p. 25—42). He found that the pure organic substance consists of an accumulation of a colonial cyanophycean alga, very similar to the present form of Gloeocapsa. He recognised the colonies as small yellow particles of a homogeneous substance. The individual cells are not observable in consequence of advanced decomposition. Amongst these extremely altered colonies were found other colonies of an alga the cells of which are observable as nearly spherical brown corpuscles. Zalessky called the alga „Gloeocapsamorpha prisca".

It is remarkable that soft algae of so great antiquity are preserved in such an excellent state and that by the action of chloralhydrate they swell and take up their original form.

The kukersite is interstratified with limestones of marine origin and itself contains also a marine fauna. This proves the marine origin of kukersite, probably it was formed in shallow bays or gulfs.

The kukersite cannot be called an oil shale. A true oil shale „is indissolubly connected with free petroleum and has been formed by specially absorbent bands of argillaceous material becoming inpregnated with the inspissated residues of liquid hydrocarbons which they retain both by chemical and mechanical combination".

(A Treatise on British Mineral Oil. Edited by J. A. Greene 1919 p. 6).

H. v. Winkler defined it as a „first step of brown coal". This is not the case. The kukersite does not contain any free bitumen and the oils can be obtained from it only by destructive distillation. According to Potanié's classification of the rocks of organic origin it is a sapropelite, really a saprocoll of a greater age. (H. Potanié, Jahrb d. Pr. geol. Landesamt. 24.

(1903) and 25. 1905. p. 353.) As the mineral is of a distinctive character Zalessky proposed to call it „kukersite".

Probably 3 processes took place side by side during its formation; 1, decomposition of the original organic matter 2, oxidation of decomposition products and 3, adsorption. In these processes adsorption determines the final chemical nature of the raw kukersite. It is well known that on filtering through Fuller's earth, colloidal clay, etc., unsaturated compounds are retained but paraffins and saturated hydrocarbons pass through freely. The great percentage of unsaturated hydrocarbons, especially the formolite forming compounds in the low-temperature kukersite tar suggest that the organic substance in the kukersite probably consists of compounds of a similar nature. It was observed by Herr that on filtering Baku oil through Fuller's earth all the formolite forming compounds were removed. (III report on Colloid Chemistry. London. 1920. p. 92 and Petr. 1909. 4, 1284). Probably the organic matter of kukersite consists of a mixture of unsaturated open chain and cyclic hydrocarbons with a small amount of unsaturated acids and traces of paraffins.

Summary.

1) The methods adopted for the analysis of coal are not wholly applicable to the analysis of kukersite.

2) In spite of the great variation in ash content of kukersite the pure organic substance of this mineral has a nearly constant ultimate composition.

3) As shown by the extraction with solvents, the kukersite does not contain any free bitumen.

4) The largest yield of crude oil is obtained at a temperature in the neighbourhood of 600° C. (Table XV).

5) The yield of ammonium sulphate is very low.

6) The crude tar may be directly used as a fuel.

7) All fractions (especially those with higher boiling points) are oxidised on exposure to the air.

8) The composition of crude low-temperature kukersite tar is not so simple as the earlier investigators assumed. It contains a great number of olefines, unsaturated cyclic hydrocarbons and unsaturated acids. The paraffin content is very low.

9) The usual methods adopted for the refining of crude petroleum are not applicable to the refining of crude oil from kukersite.

In conclusion, the author desires to record his thanks to Prof. W. A. Bone F. R. S. for his interest in the work; to Messrs E. Sinkinson D. I. C. and W. E. Stockings M. Sc. for reading the manuscript; to Prof. J. S. Philip D. Sc. for his kindness in allowing him to use the Abbe's Refractometer; to M-r J. Kopwillem, Chargé d'Affaires of the Esthonian Legation in London, for storing the samples of kukersite and finally to the Council of the University of Tartu (Esthonia) for financial support.

The Imperial College of Science and Technology,
S. Kensington, London SW. 7.

May 1921.